

PATENT ABSTRACTS OF JAPAN

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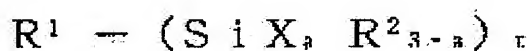
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(54) COLD-CURING COMPOSITION

(57)Abstract:

PURPOSE: To obtain a cold-curing compsn. with a low viscosity, a high elongation, and excellent strengths by mixing an org. polymer having a silicon-contg. group with a tin (II) carboxylate and an acidic and/or basic compd.

CONSTITUTION: A cold-curing compsn. is prepd. by mixing 100 pts.wt. org. polymer of the formula (wherein R1 is a residue of an org. polymer having a number-average mol.wt. of 5,000 or higher; R2 is a 1-20C monovalent hydrocarbon group; X is a hydrolyzable group; a is 1-3; and n is an integer) having, on average, at least 0.3 silicon-contg. group per molecule, 0.001-10 pts.wt. tin (II) carboxylate, and 0.001-10 pts.wt. acidic and/or basic compd. R1 in the formula is a residue of a polyoxyalkylene polymer having a ratio of the wt.-average to the number-average mol.wt. of 1.5 or lower and is pref. formed by polymerizing an alkylene oxide using a double metal cyanide complex as the catalyst. Pref. examples of the acidic and/or basic compd. are an org. amine compd. and an arom. sulfonic acid compd.



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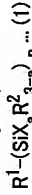
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CLAIMS

[Claim(s)]

[Claim 1] Organic polymer (A) 100 weight section which a monad is expressed with a following general formula (1), and has 0.3 or more silicon content groups per monad by total molecule average, A room-temperature-curing nature constituent containing carboxylate (B) 0.001 - 10 weight section of at least 1 and an acidic compound which are chosen from divalent tin carboxylate, divalent lead carboxylate, and bismuth carboxylate, and/or basic compound (C) 0.001 - 10 weight section.



(R¹ in a formula is the residue of a with a number average molecular weights of 5000 or more organic polymer.) A hydrocarbon group univalent [substitution of the carbon numbers 1-20, or unsubstituted] in R². X is a hydrolytic basis. a is 1, 2, or 3. n is an integer.

[Claim 2] A room-temperature-curing nature constituent of claim 1 5000 or more number average molecular weights, and whose weight average molecular weight/number average molecular weight (it is hereafter considered as M_w/M_n) R¹ in the above-mentioned general formula (1) is the residue of 1.5 or less polyoxyalkylene polymer.

[Claim 3] A room-temperature-curing nature constituent of claim 2 which is the residue of a

polyoxyalkylene polymer produced by R¹ in the above-mentioned general formula (1) polymerizing alkylene oxide in an initiator by making a composite metal cyanide complex into a catalyst.

[Claim 4] A room-temperature-curing nature constituent of claim 3 which is at least one sort as which alkylene oxide is chosen from ethylene oxide, propylene oxide, and butylene oxide.

[Claim 5] A room-temperature-curing nature constituent of claim 1 an acidic compound and/or whose basic compound (C) are organic amine compounds.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the room-temperature-curing nature constituent hardened under hygroscopic-surface-moisture existence.

[0002]

[Description of the Prior Art] The method of hardening various kinds of polymers which have an end hydrolytic silicon group which is known as conventional, for example, modified silicone, system resin, and using it for a sealing material, adhesives, etc. is known well, and is a useful method industrially.

[0003]

[Problem(s) to be Solved by the Invention] The publicly known polymer which has such an end hydrolytic silicon group is proposed by JP,45-36319,B, JP,46-17553,B, JP,61-18582,B, etc., for example.

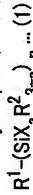
[0004] Among the polymers which have an end hydrolytic silicon group, especially, with the compound which has alkoxy silyl groups as a hydrolytic silicon group, in order to give room-temperature-curing nature, using what is called a curing catalyst is usually performed.

[0005] As such a curing catalyst, although metal salt, an acidic compound, or a basic compound of carboxylic acid, etc. is generally known, carboxylate of a tetravalent organotin compound or divalent tin is especially common. The combination with divalent tin carboxylate, acidic compound, or basic compound indicated especially to JP,61-60867,B is a very effective method from the compression set nature of a hardened material being improved remarkably, when it is used as a catalyst for 2 liquid sealing agents.

[0006] However, combination with carboxylate of divalent tin, an acidic compound, or a basic compound is used as a catalyst. The polymer which has the hydrolytic silicon group manufactured by the method of introducing a hydrolytic silicon group after a dihalogen compound's tying the polyether compound of the comparatively short molecular weight proposed by the aforementioned well-known example, setting it and carrying out polymers quantification, when the mixture which consists of bulking agents etc. was stiffened and the amount of the catalyst used that required working life is obtained was used, there was a fault to which the manifestation of the hardness of the whole depths hardenability, i.e., a hardened material, worsens.

[0007]

[Means for Solving the Problem] This invention tends to cancel such a fault and a monad is expressed with a following general formula (1). And organic polymer (A) 100 weight section which has 0.3 or more silicon content groups per monad by total molecule average. It is a room-temperature-curing nature constituent containing carboxylate (B) 0.001 - 10 weight section of at least 1 and an acidic compound which are chosen from divalent tin carboxylate, divalent lead carboxylate, and bismuth carboxylate, and/or basic compound (C) 0.001 - 10 weight section.



(R^1 in a formula is the residue of a with a number average molecular weights of 5000 or more organic polymer.) A hydrocarbon group univalent [substitution of the carbon numbers 1-20, or unsubstituted] in R^2 . X is a hydrolytic basis. a is 1, 2, or 3. n is an integer.

[0008] As for R^1 in the above-mentioned general formula (1), it is preferred that 5000 or more number average molecular weights and M_w/M_n are the residue of 1.5 or less polyoxyalkylene polymer.

[0009] Although 5000 or more number average molecular weights and M_w/M_n are manufactured using a specific catalyst, for example, a composite metal cyanide complex, a porphyrin complex, etc., 1.5 or less polyoxyalkylene polymer, A polyoxyalkylene polymer especially produced by polymerizing alkylene oxide in an initiator by making a composite metal cyanide complex into a catalyst is preferred. This polyoxyalkylene polymer has a preferred thing of a hydroxyl group end which makes monoepoxide, such as alkylene oxide, etc. react to initiators, such as a hydroxy compound which has at least one hydroxyl group under existence of a catalyst, and manufactures.

[0010] A polyoxyalkylene polymer manufactured using a composite metal cyanide complex catalyst etc. has M_w/M_n narrower than a polyoxyalkylene polymer manufactured using the conventional alkaline metal catalyst, and hypoviscosity-ization can be realized more in the amount of polymers as compared with the former.

[0011] As for a functional group number of this polyoxyalkylene polymer, two or more are preferred, and 2-4 are especially preferred. As a polyoxyalkylene polymer, a polyoxyethylene compound, a polyoxypropylene compound, a polyoxybutylene compound, a polyoxyhexylene compound, polyoxytetramethylen compounds, and/or these copolymers are specifically mentioned.

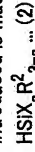
[0012] Especially desirable polyoxyalkylene polymers are polyoxypropylene diol, polyoxypropylene triol, and polyoxypropylene tetraol. When using for a method of the following (b) or (**), a polyoxyalkylene polymer of olefin ends, such as an allyl end polyoxypropylene monooar, can also be used.

[0013] R^2 in a general formula (1) is a univalent organic group substitution of the carbon numbers 1-20, or unsubstituted, and is a with a carbon number of eight or less alkyl group, a phenyl group, and a fluoro alkyl group preferably. They are a methyl group, an ethyl group, a propyl group, a propenyl group, a butyl group, a hexyl group, a cyclohexyl group, a phenyl group, etc. especially preferably.

[0014] X in a general formula (1) is a hydrolytic basis, for example, there are a halogen atom, an alkoxy group, an acyloxy group, an amide group, an amino group, an aminoxy group, a KETOKISHI mate group, an acid-amide group, a hydride group, etc. As for a carbon number of a hydrolytic basis which has a carbon atom among these, six or less are preferred, and four especially or less are preferred. The desirable hydrolytic basis can illustrate a with a carbon number of four or less lower alkoxy group especially a methoxy group and an ethoxy basis, a propoxy group, a propenyl group, etc. a in a general formula (1) is 1, 2, or 3, and it is preferred that it is especially 2 or 3.

[0015] Next, a manufacturing method of an organic polymer (A) is explained. As for an organic polymer (A) in this invention, what introduces a silicon content group into an end of a polyoxyalkylene polymer which has a functional group so that it may state below, and is manufactured is preferred. Such a compound is liquefied at a room temperature, and when a hardened material holds adaptability and uses for a sealing material, adhesives, etc. also at low temperature comparatively, it is provided with the desirable characteristic.

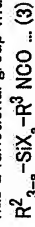
[0016] (**) A method to which a hydrosilyl compound expressed with an end of a polyoxyalkylene polymer which has a functional group with a following general formula (2) that an olefin group was introduced is made to react.



(R^2 in a formula, X, and a are the same as the above.)

As a method of introducing an olefin group here, A compound which has an unsaturation group and a functional group is made to react to terminal hydroxyl groups of a polyoxyalkylene polymer. How to combine by ether bond, ester bond, a urethane bond, carbonate combination, etc., Or when polymerizing alkylene oxide, a method of introducing an olefin group into a side chain, etc. are mentioned by adding and carrying out copolymerization of the olefin group content epoxy compounds, such as allyl glycidyl ether.

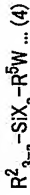
[0017] (**) A method to which a compound expressed with an end of a polyoxyalkylene polymer which has a functional group with a following general formula (3) is made to react.



(R^2 in a formula, X, and a are the same as the above.) R^3 --- divalent hydrocarbon group of the carbon numbers 1-17.

[0018] (**) A method to which W basis of a silicon compound expressed with a following general formula (4) to this isocyanate group is made to react after making polyisocyanate compounds, such as tolylene diisocyanate, react to an end of a polyoxyalkylene polymer which has a functional group

and considering it as an isocyanate group end.



(R^4 in a formula, R^5 , X, and a are the same as the above.) Active hydrogen containing group as which W was chosen from a hydroxyl group, a carboxyl group, a sulfinyl group, and an amino group (the 1st class or the 2nd class).

[0019](*)A method which introduces an olefin group into an end of a polyoxyalkylene polymer which has a functional group and to which the olefin group and a sulfinyl group of a silicon compound expressed with a general formula (4) whose W is a sulfinyl group are made to react.

[0020]A silicon content cardinal number is 0.3 or more per monad in a total molecule average.

[0021]As an organic polymer (A) in the invention in this application, an organic polymer of the number average molecular weight 5000-30000 can be used. If elongation will become low and a number average molecular weight exceeds 30000 firmly [a hardened material] when a number average molecular weight of this organic polymer is lower than 5000, pliability and elongation of a hardened material are satisfactory, but viscosity of the polymer itself [this] becomes remarkably large, and practicality becomes low. As for especially a number average molecular weight, 8000-30000 are preferred.

[0022]Although it is indispensable to use a curing catalyst in this invention, carboxylate (B), an acidic compound, and/or a basic compound (C) of at least 1 which are especially chosen from divalent tin carboxylate, divalent lead carboxylate, and bismuth carboxylate are used as a catalyst. Especially a desirable thing is divalent tin carboxylate and/or bismuth carboxylate as carboxylate (B), and these may be independent or may be used as a mixture. In this invention, these metal carboxylate (B), an acidic compound, and/or a basic compound (C) are used together as a catalyst.

[0023]Specifically as divalent tin carboxylate of this invention, an aliphatic-carboxylic-acid salt of tin like octyloxy acid tin, lauryl acid tin, and stearic acid tin is mentioned. An aliphatic-carboxylic-acid salt of tin like lead octylate, lauryl ****, and lead stearate as divalent lead carboxylate is mentioned. As bismuth carboxylate, aliphatic series and/or alicyclic follows carboxylic acid of bismuth, such as octyloxy acid bismuth and a bismuth BASA rate (mixed fatty acid salt), are mentioned.

[0024]As an acidic compound of this invention, an acidic compound like organic acid or inorganic acid can be used. An organic carboxylic acid compound and an organic-sulfonic-acid compound are preferred also in especially inside. Specifically, aromatic-sulfonic-acid compounds, such as aromatic carboxylic acid compounds, such as aliphatic series mono- ***** polycarboxylic acid compounds, such as formic acid, acetic acid, propionic acid, caproic acid, caprylic acid, octyloxy acid, chloroacetic acid, and succinic acid, and benzoic acid, and Para toluenesulfonic acid, are preferred. As inorganic acid, inorganic solid acid, such as chloride, nitric acid, sulfuric acid, etc. a magnesium silicate, aluminum silicate, can be mentioned.

[0025]As a basic compound, an organic amine compound is preferred and specifically Octyl amine, Aliphatic series, aromatic polyamine, etc., such as aliphatic series, such as lauryl amine, stearylamine, and aniline, and aromatic monoamine, ethylenediamine, triethylenediamine, triethylenetetramine, and a phenylenediamine, can be used. As an acidic compound and/or a basic compound (C), an organic amine compound is preferred.

[0026]As amount of curing catalyst used, organic polymer (A) 100 weight section is received, it is preferred to use 0.001 - 10 weight section, an acidic compound, and/or a basic compound (C) for metal carboxylate (B) in the range of 0.001 - 10 weight section, it is preferred that metal carboxylate (B) 0.05 - three weight sections, an acidic compound, and/or a basic compound (C) carry out 0.05-3 weight-section use especially.

[0027]The constituent of this invention can contain still more publicly known various bulking agents, a plasticizer, an additive agent, etc. As a bulking agent, can use a publicly known bulking agent, and specifically, Fumes silica, sedimentation nature silica, a silicic acid anhydride, hydrous silicic acids, and a bulking agent like carbon black. Calcium carbonate, magnesium carbonate, diatomite, calcination clay, clay, Bulking agents, such as talc, titanium oxide, bentonite, organic bentonite, ferric oxide, a zinc oxide, an active white, hydrogenation castor oil, and a milt balloon, asbestos, glass fiber, and a fibrous filler like a filament can be used.

[0028]As a plasticizer, can use a publicly known plasticizer and specifically Dioctyl phthalate, Phthalic ester, such as dibutyl phthalate and butylbenzyl phthalate; Dioctyl adipate, Glycol ester, such as aliphatic-carboxylic-acid ester; pentaerythritol ester, such as succinic acid isodecyl, dibutyl sebacate,

and butyl oleate; Trioctyl phosphate, Phosphoric ester, such as tricresyl phosphate; epoxy plasticizer; chlorinated paraffins, such as epoxidized soybean oil and epoxy stearic acid benzyl, etc. can be independent, or can use it with two or more sorts of mixtures.

[0029]As an additive agent, adhesion grant agents, such as phenol resin and an epoxy resin, paints, various kinds of antiaging agents, an ultraviolet ray absorbent, etc. can be used.

[0030]Especially a room-temperature-curing nature resin composition of this invention is carried out as an object for elastic sealant, and an object for adhesives, and can carry out like.

[0031]

[Example]Although an example explains this invention concretely below, this invention is not limited only to these examples.

[0032][Reference example 1] By a method given in JP 3-72527 A, propylene oxide is polymerized with a zinchexacyano cobaltate catalyst by using the diethylene glycol propylene oxide addition of the molecular weight 1000 as an initiator, Polyoxypropylene diol of the number average molecular weight 19000 ($M_w/M_n=1.10$) is obtained, Terminal hydroxyl groups is changed into allyl ether groups, the addition reaction of the methyl dimethoxysilane was further carried out by having made chloroplatinic acid into the catalyst, and the organic polymer (P1) which has an average of 1.6 hydrolytic silicon groups per molecule was obtained.

[0033][Reference example 2] By a method given in JP 3-72527 A, propylene oxide is polymerized with a zinchexacyano cobaltate catalyst by using the glycerin propylene oxide addition of the molecular weight 100 as an initiator, Polyoxypropylene triol of the number average molecular weight 15000 ($M_w/M_n=1.10$) is obtained, Terminal hydroxyl groups is changed into allyl ether groups, the addition reaction of the methyl dimethoxysilane was further carried out by having made chloroplatinic acid into the catalyst, and the organic polymer (P2) which has an average of 1.4 hydrolytic silicon groups per molecule was obtained.

[0034][Reference example 3] Change into allyl ether groups the terminal hydroxyl groups of the polyoxypropylene diol of the number average molecular weight 10000 ($M_w/M_n=1.10$) obtained like the reference example 1, and the addition reaction of the methyl dimethoxysilane is further carried out by making chloroplatinic acid into a catalyst. The organic polymer (P3) which has an average of 1.2 hydrolytic silicon groups per molecule was obtained.

[0035][Reference example 4] By a method given in JP 3-72527 A, propylene oxide is polymerized with a zinchexacyano cobaltate catalyst by using pentaerythritol as an initiator, Polyoxypropylene tetraol of ($M_w/M_n=1.10$) of the number average molecular weight 18000 is obtained, Terminal hydroxyl groups is changed into allyl ether groups, the addition reaction of the methyl dimethoxysilane was further carried out by having made chloroplatinic acid into the catalyst, and the organic polymer (P4) which has an average of 2.6 hydrolytic silicon groups per molecule was obtained.

[0036][Reference example 5] Polyoxypropylene diol of the number average molecular weight 4000 is made to react to bromochloromethane based on a method given in JP 61-49332 B. After making terminal hydroxyl groups react to allylchloride furthermore and considering it as end allyl ether groups, the addition reaction of the methyl dimethoxysilane was further carried out by having made chloroplatinic acid into the catalyst, and the organic polymer (P5) was obtained. The number average molecular weight of polyoxypropylene pyrenediol conversion of this organic polymer was 11000 ($M_w/M_n=1.7$).

[0037][Reference example 6] To dioctylacid tin 100 weight section, lauryl amine 30 weight section could be added, it mixed, and the catalyst mixture (C) was obtained.

[0038][An example and comparative example] A catalyst mixture (C) to polymer (P1-P5) 100 weight section compounded by the reference examples 1-5 1 weight-section ***** Under [after recuperating oneself for the bottom of 25 ** and a 60% humidity condition, and seven days] 50 ** and a 60% humidity condition, it was recuperated for seven days and (%), ductility, and polymer viscosity (based on 25 ** and BH type viscosity meter) (cps) were measured at the time of intensity (kg/cm^2) and a fracture at the time of a 50% modulus (M_{50}) (kg/cm^2) and a fracture. It collects into

Table 1.

[0039]To polymer (P1-P5) 100 weight section, calcium carbonate 160 weight section, Titanium oxide 20 weight section, dioctyl phthalate 60 weight section, hydrogenation castor oil 5 weight section, after adding and kneading phenolic antioxidant 1 weight section, finger touch tack free time becomes

in 4 hours about the catalyst mixture (C) obtained by the reference example 6 in a 23 °C thermostatic chamber — as — an initial complement (a weight section.) Table 1 — being shown — it added, and mixed well, they were neglected under ordinary temperature, and the hardness of the hardened material of one day, two days, three days, and seven days after was measured. However, sample thickness was measured at 1 cm, the hardness scale C2 type made from a polymers meter, and 23 °C. A result is shown in Table 1.

[0040]

[Table 1]

使用重合体	P 1	P 2	P 3	P 4	P 5
M _n	1. 1	1. 3	1. 3	1. 3	1. 1
硬化時強度	4. 6	4. 4	4. 7	4. 4	4. 2
硬化時粘度	360	300	360	300	310
重合体粘度	16000	10000	8000	10000	14000
硬化物硬度					
1日後	27	29	28	29	15
2日後	29	31	30	31	19
3日後	30	32	32	33	23
7日後	30	32	32	33	29
触媒添加量	3	3	2. 8	2. 8	3. 5

[0041]

[Effect of the Invention]The room-temperature-curing nature constituent which uses as a hardening component the hydrolytic silicon group content organicity polymer which has intrinsically the polyoxyalkylene polymer produced by using the composite metal cyanide complex catalyst of this invention, and polymerizing alkylene oxide in an initiator in a main chain. It has the effect of having the outstanding elongation and strength properties, and low viscosity as compared with the polymer which carries out chain extension of the polymer of comparatively a low number average molecular weight known conventionally, and manufactures it.

[Translation done.]